Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative

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Hard Chrome Plating
(Why do we use it?)

- **Why Chrome plating?**

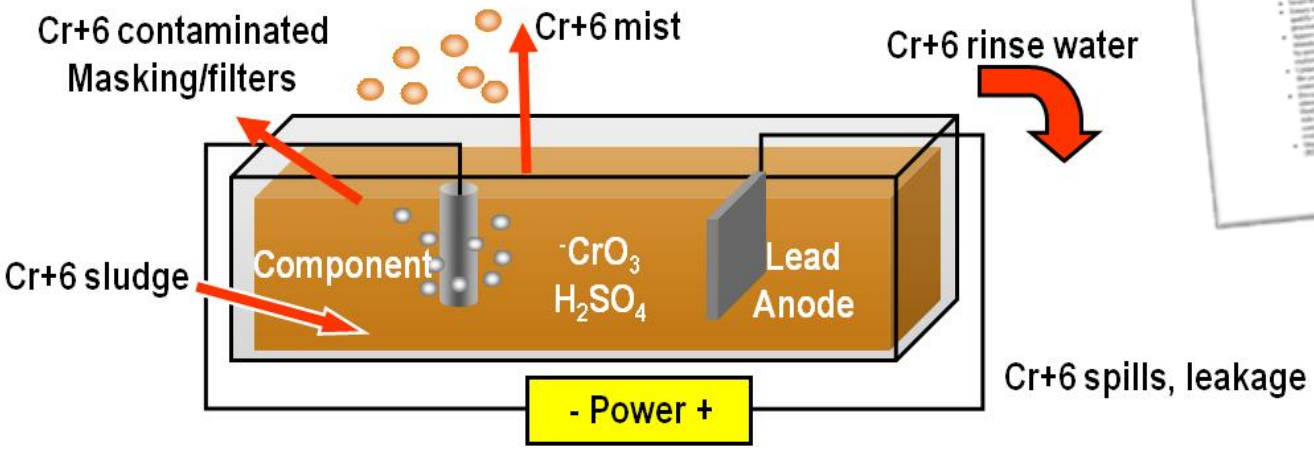
  Engineering hard chrome (EHC) coatings are used extensively in both industry and military applications due to their excellent performance characteristics.
  - Wear
  - Corrosion Resistance
  - Dimensional Restoration

- **Where is Chrome Plating Used?**
  - Manufacturing and repair
  - Dynamic components
  - Hydraulic actuators
  - Propeller hubs
  - Engines
  - Landing Gear

Hard Chrome Plating
(The Problem)

- **Hard Chrome Plating Environmental & Health Hazards**
  - Hard chrome plating utilizes chromium in the hexavalent state (Cr^{6+})
  - Cr^{6+} is a known carcinogen and poses a health risk to operators
  - OSHA lowered the Cr^{6+} PEL from 52 µg/m^3 to 5 µg/m^3

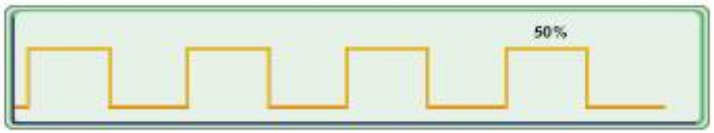
- **8 Apr 09, Memorandum, DoD Directive**
  - Hexavalent Chromium Management Policy
  - NAVAIR Cr^{6+} Authorization Process



Hard Chrome Alternative

INTEGRAN Nanovate™ CR

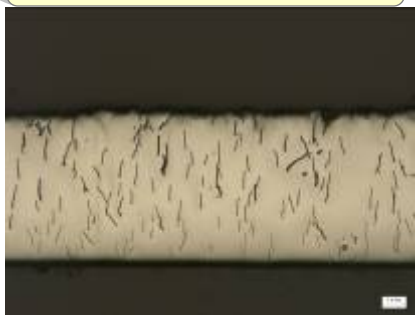
- **Coating applied by electrodeposition**
  - Pulsed Current Waveform Engineering
    - Frequency (Hz) = $1/(t_{on}+t_{off})$
    - Duty Cycle (%) = $t_{on}/(t_{on}+t_{off})x100$



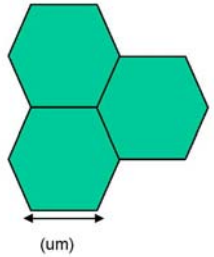
- **Electrodeposited nanocrystalline materials**
  - Favors nucleation of new grains over growth
  - Results in an ultra-fine grain structure
  - Uniform throughout thickness
- **Leads to unique properties**
  - ↑ Yield Strength, wear, ultimate tensile strength
  - ↑ Density
  - ↓ Coefficient of friction

(Smaller grain size impedes dislocation movement and increases yield strength)

Hard Chrome Deposit

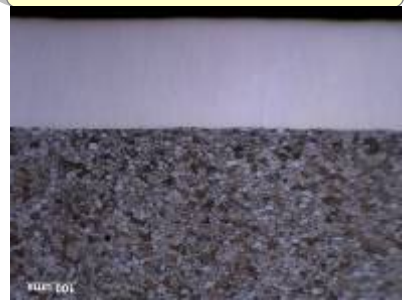


Cross section of typical EHC deposit showing macro cracks. Average grain sizes of 10 – 100 µm.



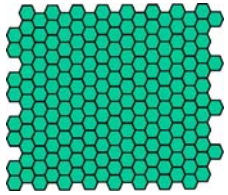
Polycrystalline (10-100 µm)

*Nanovate™ CR



Cross section of Nanovate™ CR deposit. Process creates electrodeposits with grains of 20 nm or less (1000 times smaller).

**Nanocrystalline Co-P Deposit*



Nanocrystalline (< 100 nm)

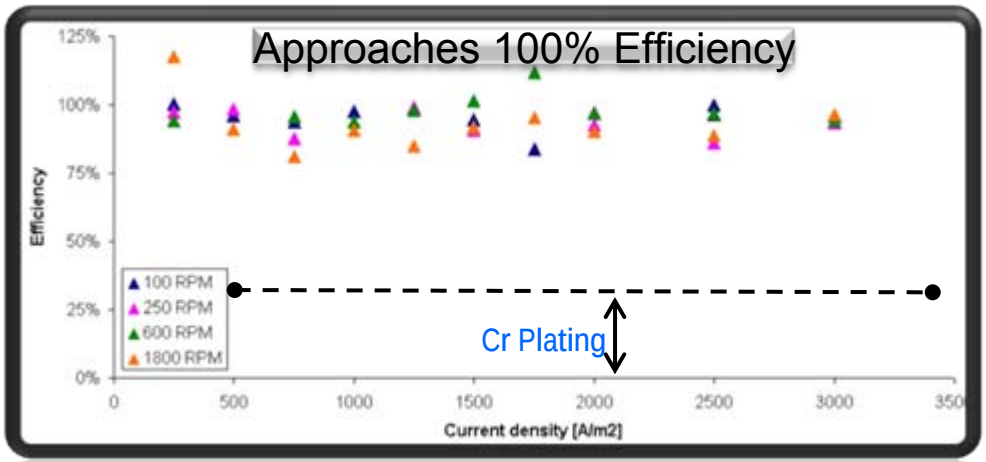
Hard Chrome Alternative

Nanovate™ CR

Process Comparison

	Nanovate™ CR	EHC
Deposition Method	Electrodeposition (Pulse)	Electrodeposition (DC)
Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002”-0.008” /hr	0.0005”-0.001” /hr
Emission Analysis	*Below OSHA limits	Cr+6

Cathode Efficiency



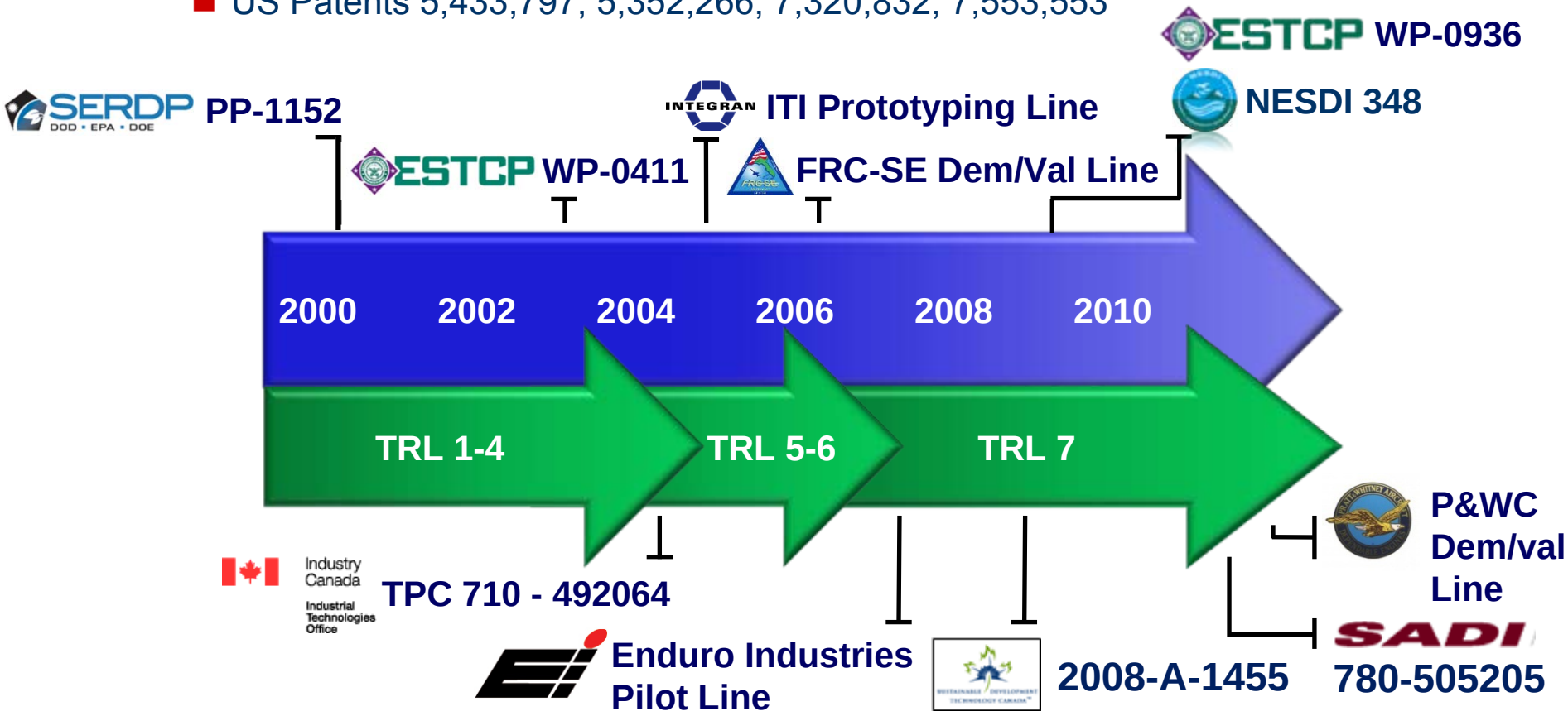
Nanovate™ CR Plating Tank at FRCSE

- Up to 8X faster than Chrome plating
- Increased throughput
- One Nanovate CR tank can replace several EHC tanks
- More efficient (~ 90% Reduced power consumption)
- Bath is Stable

**Co PEL is 20 µg/m3*

Technology Development

- Developed and demonstrated at the lab scale
- Scaled up to industrial production & moved to DoD depot
- US Patents 5,433,797, 5,352,266, 7,320,832, 7,553,553



Technology Dem/Val Site
(Full Operating Capability)

CIP # 0466

- **NAVAIR Fleet Readiness Center Jacksonville**
  - Dem/Val line in operation since 2006
  - 250 gallon Plating Tank
  - Pulse Power supply (1500A Peak Current)
  - Activation tank used for most all alloys

Dem/Val Plating Tank

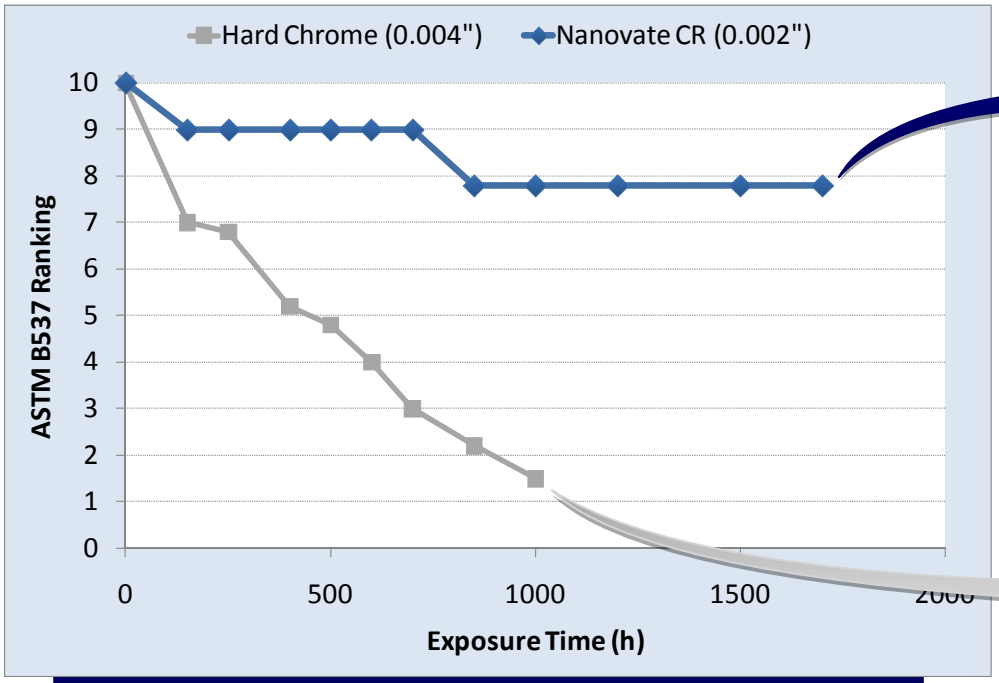
Power Supply

Remote Controller

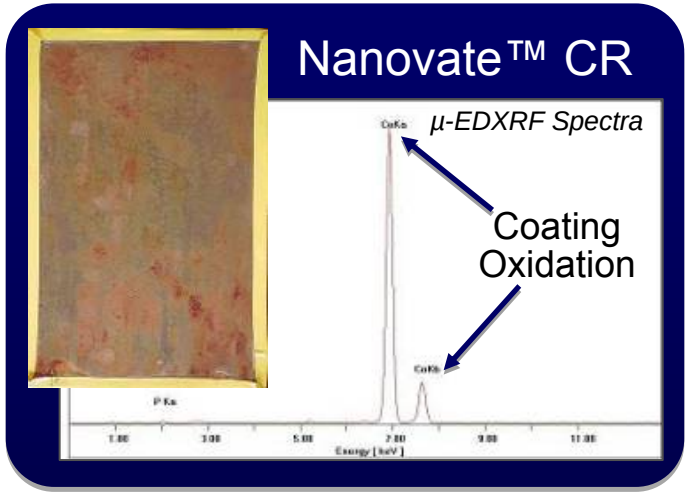
Acid/Fluoride Activation tank

Corrosion Properties

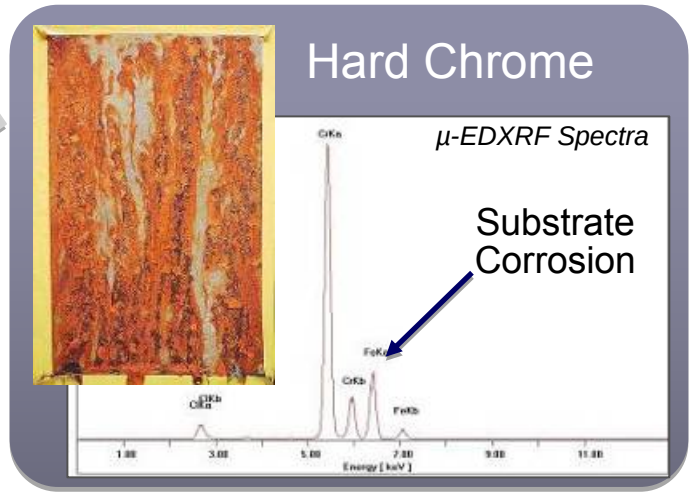
Nanovate™ CR



ASTM B537 Ranking following ASTM B117 Salt Spray

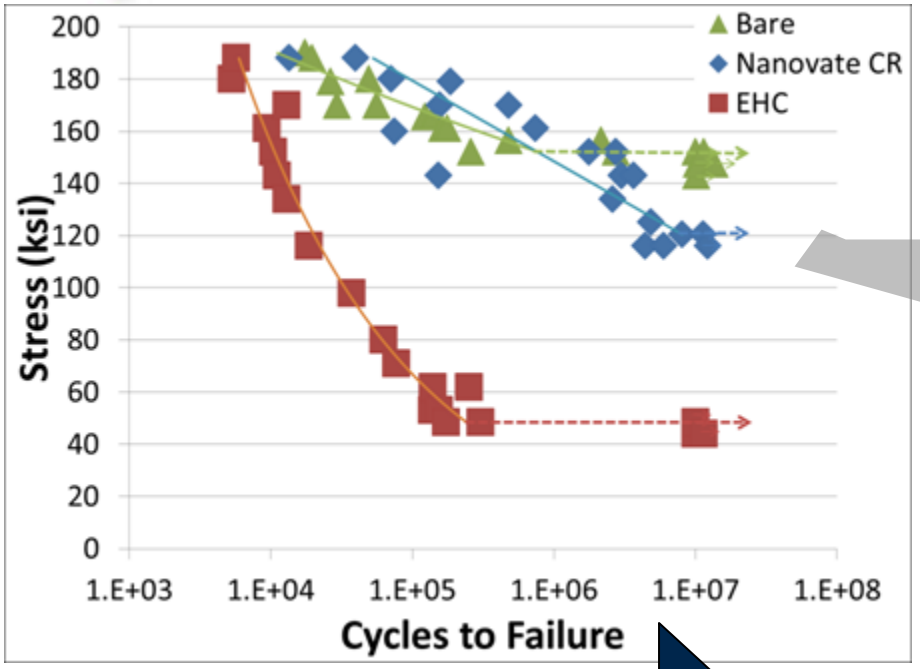


** Photos shown following 165 hrs*



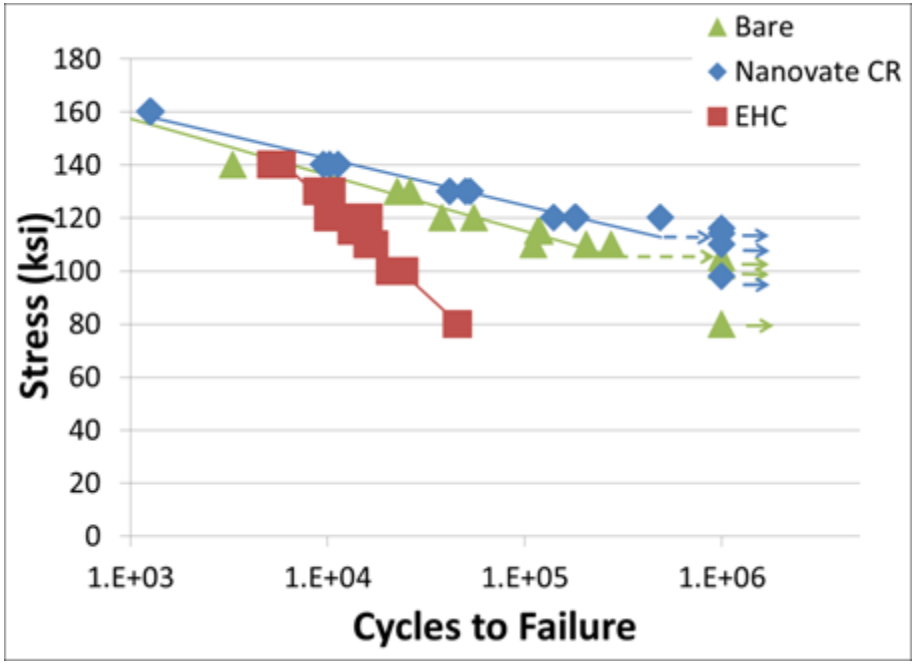
Fatigue Properties

Nanovate™ CR



Rotating Beam Fatigue
4340 substrate (UTS: 260-280 ksi)
Significant credit vs. EHC
Comparable to bare

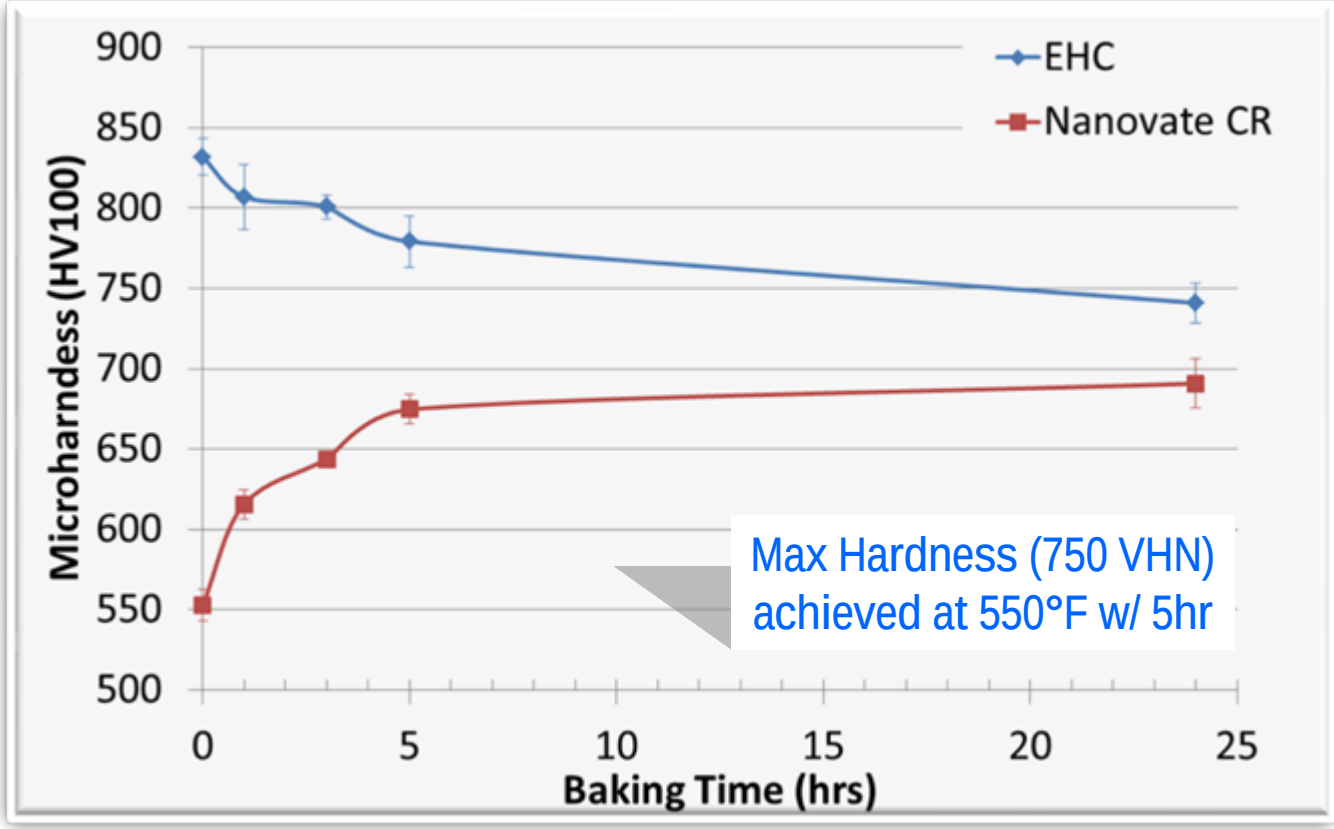
Axial Fatigue (R=-1)
4340 substrate (UTS: 180-200 ksi)
Significant credit vs. EHC
Credit vs bare



Hardness Properties

Nanovate™ CR

Nanovate CR hardness comparable to EHC after annealing at standard conditions for hydrogen embrittlement bakeout (375°F)



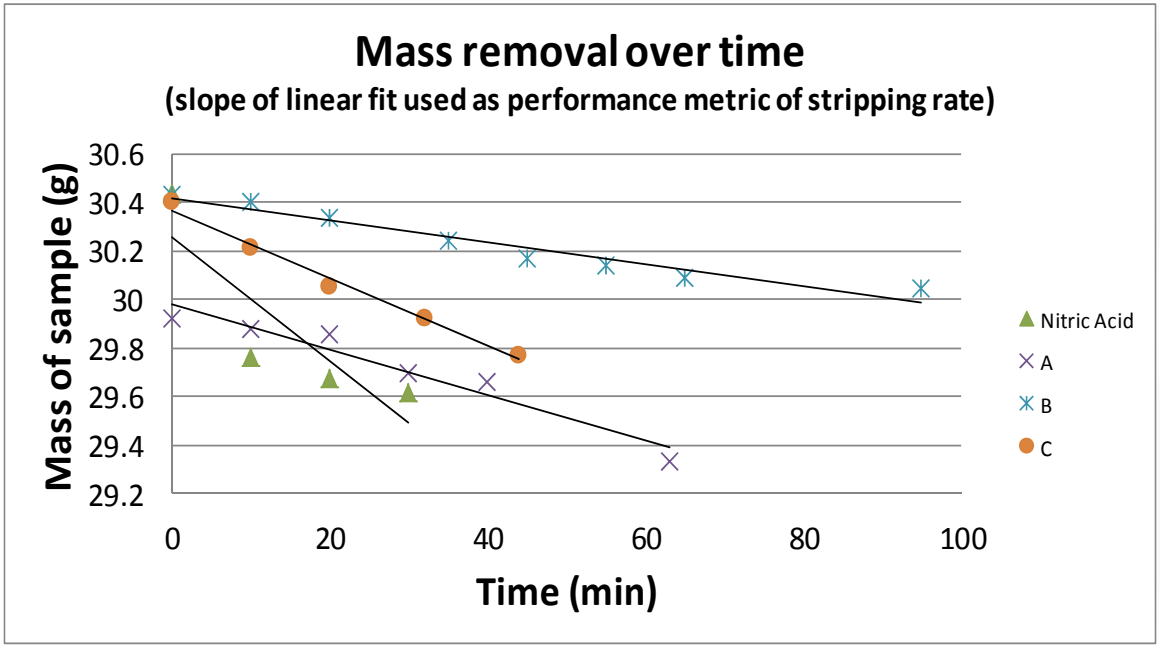
Technical Progress
(Masking Evaluation)

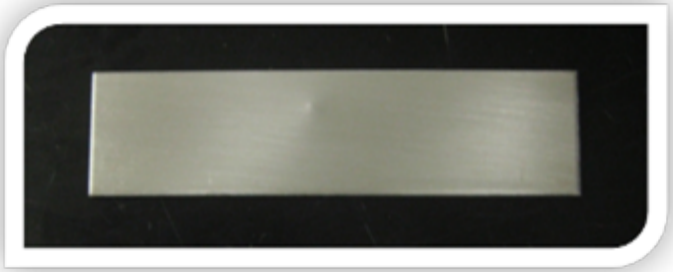
- Maskants evaluated and downselected
  - Enthone: Enplate Stop Off No. 1
  - Tolber: Microshield
- No adverse effects on bath or deposit quality
- Demonstrated on T45 pivot component

T-45 pivot shown with Enthone Maskant

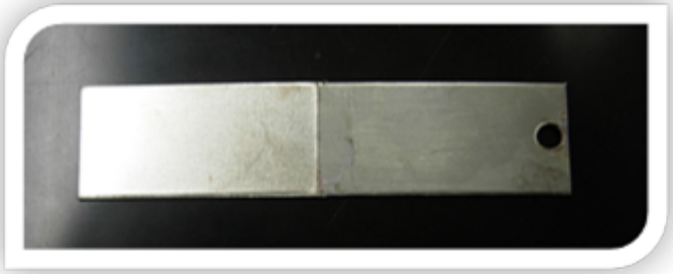
Technical Progress
(Coating Removal Evaluation)

- **Strippants evaluated and downselected**
  - (3) nitro-organic oxidizers with amino compounds
- **0.001”-0.004”/hr removal rates**
- **MacDermid METEX SCB Electroless Nickel Stripper was tested at JAX successfully.**

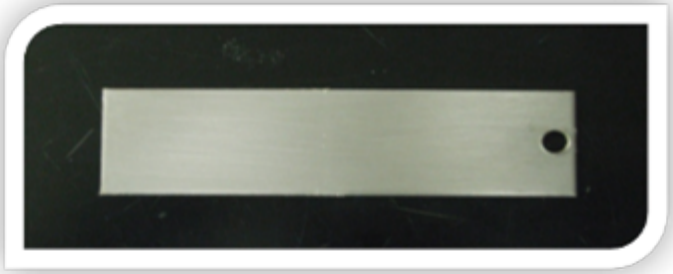




Pre-plate coupon



Plated coupon



Stripped coupon

Technology Dem/Val at JAX
(JTP Progress)

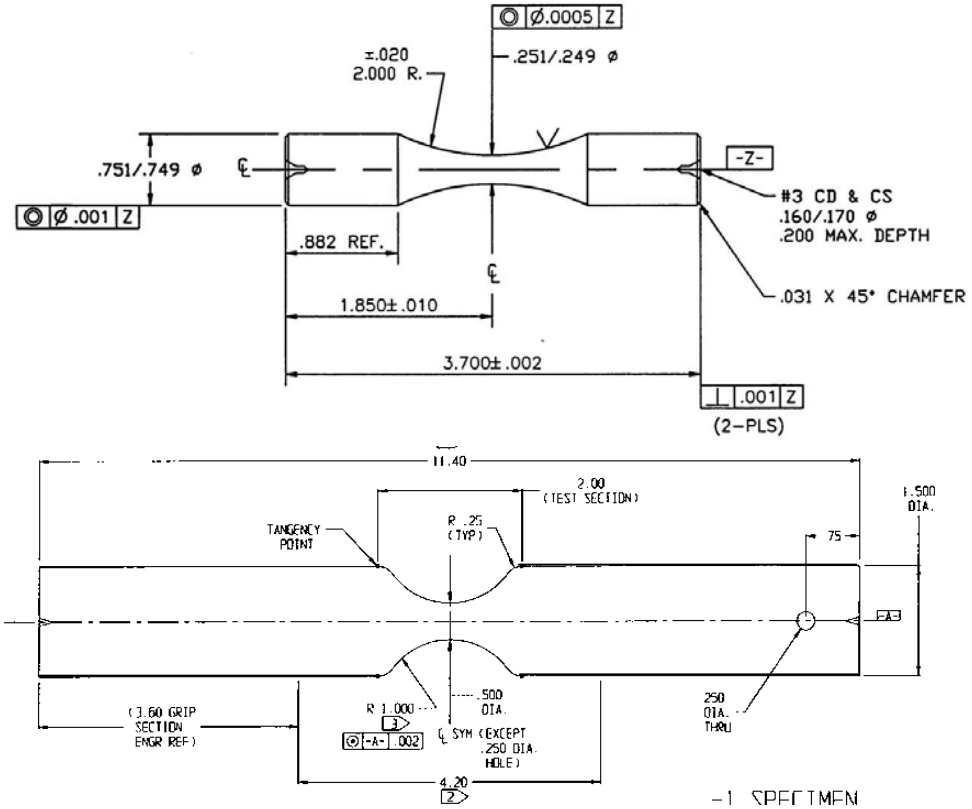
WP-0936 – Feb 2011

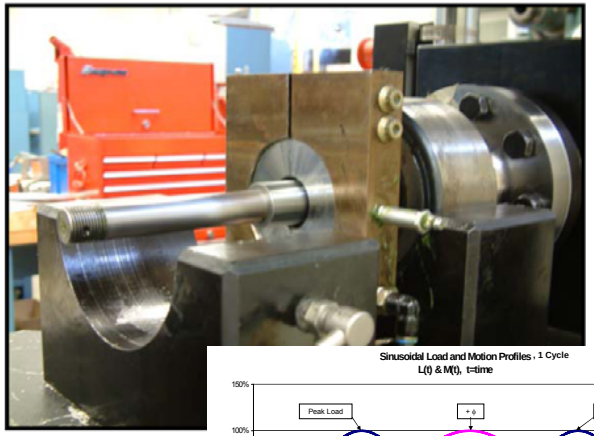
ESTCP JTP & Dem/Plan

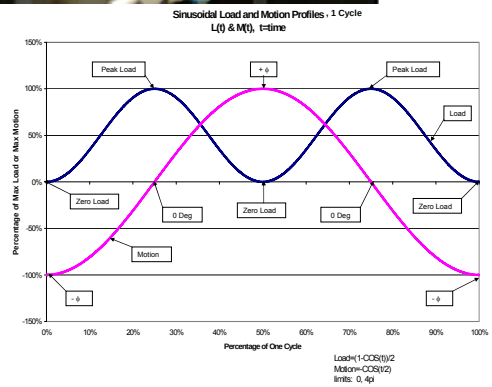
24 Core Tests Defined in JTP

- Coating Quality
  - Appearance, Thickness, Porosity, Hardness, Grain size
- Ductility
- Stress (internal)
- Fatigue (Axial)
- Corrosion (B117, SO_2, Beach. OCP)
- Adhesion
- HE, HRE
- Fluid Compatibility
- Wear
  - (Taber, PoD, Rig, Falex, Gravelometry, SATEC)

Fatigue/Wear Testing







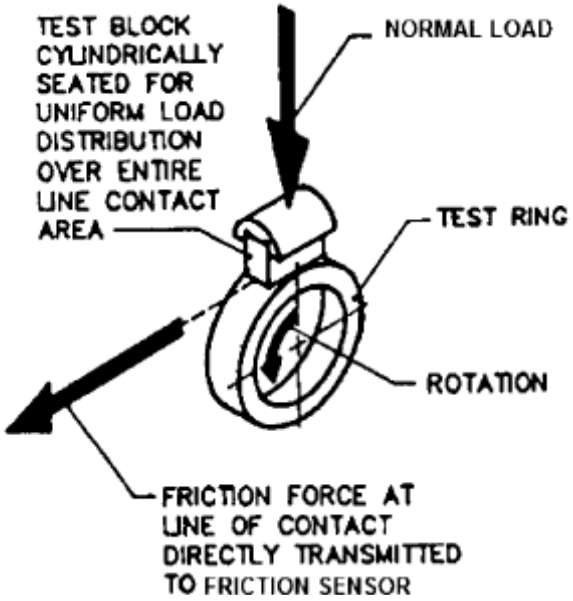
Axial Fatigue Test

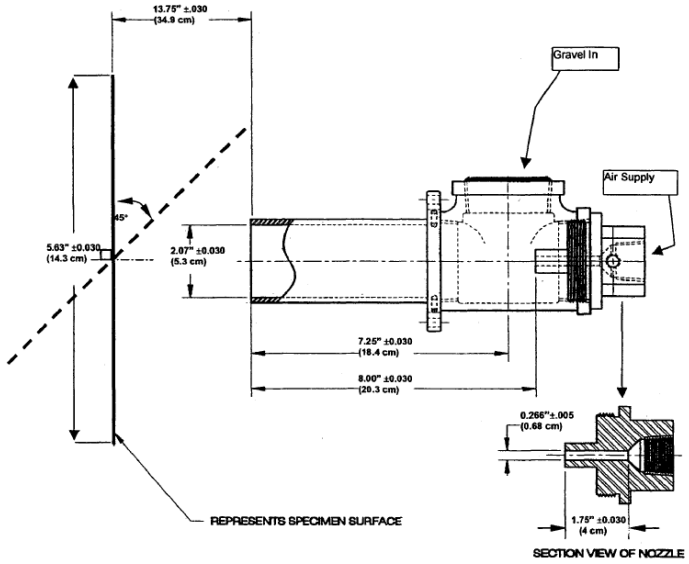
- 4340 steel (260-280 ksi)
- Shot peened
- R ratio: R = -1

SATEC Oscillating Load Test

- Boeing Specific Test
- Pin/Bushing Oscillating Wear Test
- Constant/ Sinusoidal load-motion profile

Wear Testing





FALEX Block on Ring

- Test per ASTM G77
- determines the resistance of materials to sliding wear
- Different Alloy/Coatings against Ring

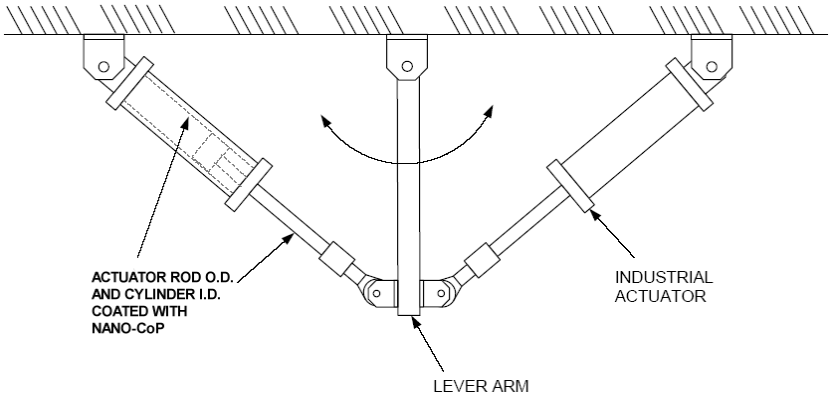
Gravelometry

- Test per ASTM D3170
- Specimens mounted perpendicular to projected path
- Pea size gravel; air pressure 70 psi

Endurance Rig Testing

Messier-Dowty
SAFRAN Group

- **Assess wear performance vs. chrome as an ID actuator**
- **Test developed by Messier-Dowty**
  - 20,000 Cycles
  - Observe the effect of surface finish, seal types, and hardening condition



Endurance Test Rig Schematic

Test Matrix*

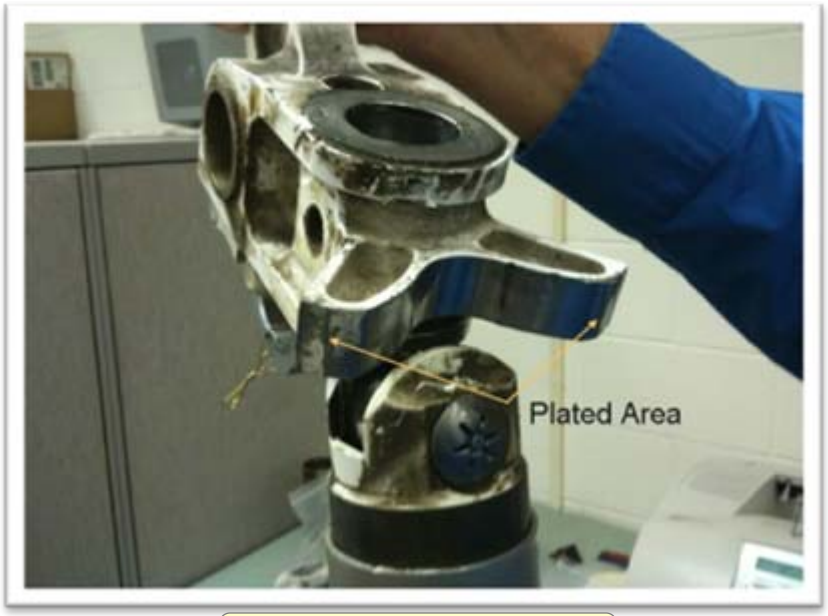
Coating	Surface Finish (Microinches)	Piston Seal	Rod Seal
EHC	12-16	Buna-N Tee Seal Nitrile Butadiene Rubber	Buna-N Tee Seal Nitrile Butadiene Rubber
EHC	4-6		
nCoP	12-16		
nCoP	4-6		
nCoP HE Bake	12-16		
nCoP HE Bake	4-6		
nCoP Hardening Heat Treat	12-16		
nCoP Hardening Heat Treat	4-6		
EHC	12-16	Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer	Viton Tee Seal Synthetic Rubber Fluoropolymer Elastomer
nCoP	12-16		
EHC	12-16	PTFE Cap	Spring Energized PTFE
nCoP	12-16		
EHC	12-16	Buna-N O-Ring/Back-up-Nitrile Butadiene Rubber O-Ring	Buna-N O-Ring/Back-up-Nitrile Butadiene Rubber O-Ring
nCoP	12-16		

In kind funding (Messier-Dowty)

Dem/Val Components
T-45 Pivot Assembly

NAVAIR JAX Dem/Val for Air Vehicle Components

- **T-45 Arresting Hook Pivot Assembly**

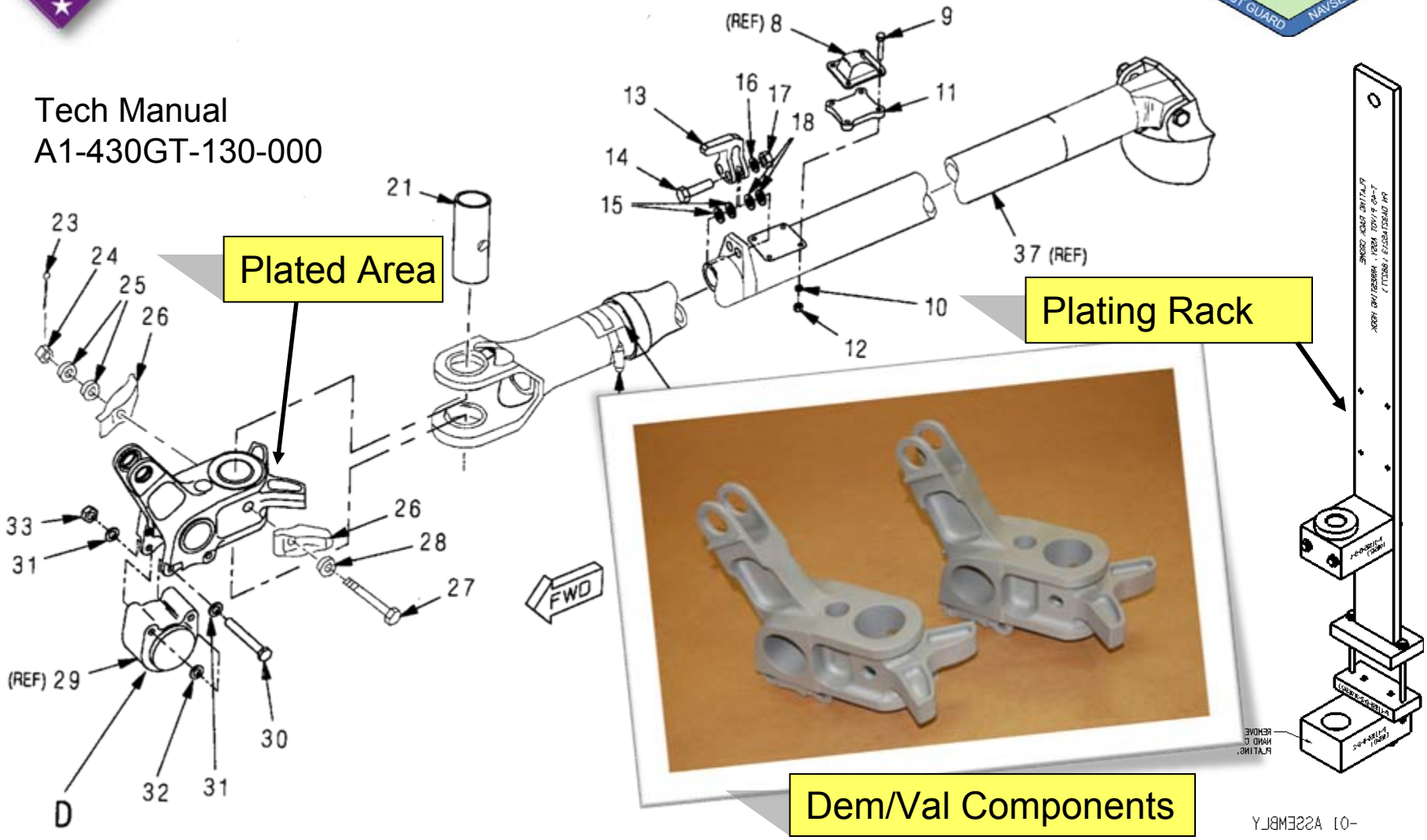


Pivot Assembly

T-45 Goshawk Trainer Aircraft

Dem/Val Components
T-45 Pivot Assembly

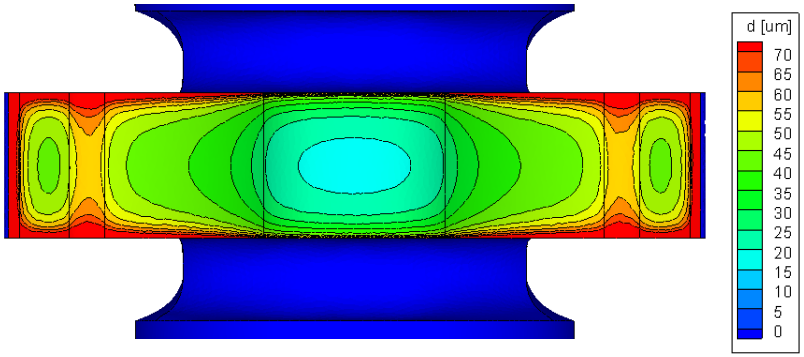
Tech Manual
A1-430GT-130-000



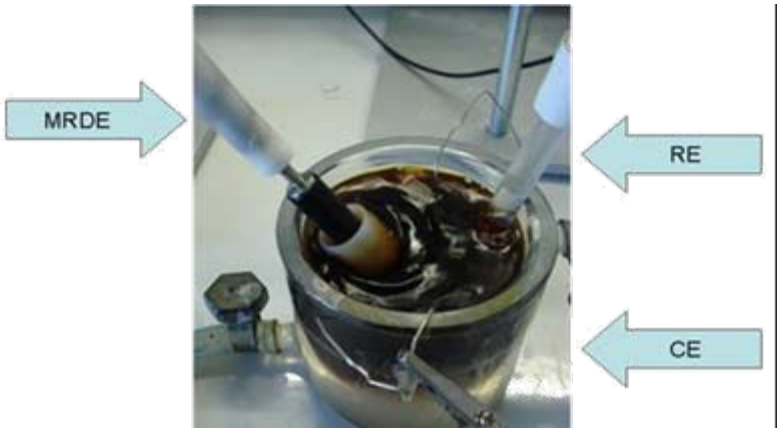
Electroplating Simulation: T-45 Pivot Assembly

Electrochemical Modeling

- Conducted chemical characterization for model input
- Optimize current density distribution
- Control composition of electroplate
- Optimize coating properties
- Applied simulation to a complex geometry – T45 Pivot Assembly



T-45 Pivot Assy



Bath Characterization

Potential Dem/Val Component Lifting Arm Pin

NAVAIR Lakehurst – Lifting Arm Pin

- Spotting Dolly- Lifting Arm Axel Pin
- EHC vs. Nanovate Cr vs. E-Ni

Various Lifting Pin Systems

Spotting Dolly Lifting Arm

NAVSEA Leveraged Effort
LVS Hydraulic Cylinder

NAVSEA (NESDI & OSD Leveraged Effort)

- **Marine Corps MK48 LVS (Logistic Vehicle System) Hydraulic Cylinders**

- (1) Evaluate coatings on steel and carburized steel laboratory panels
- (2) Evaluate optimum coatings with accelerated corrosion testing (GM9540P)
- (3) Field test on MK48 vehicles

Goals:

- Develop selection criteria for implementation into system repair / rebuild and spare parts sourcing
- Reduce corrosion maintenance requirements and repair costs of vehicles

NAVSEA Leveraged Effort
LVS Hydraulic Cylinder

- Phase I: (*Carburized 1018 Steel Coupons)
  - Unofficial test results
    - ASTM B117 (passed)
    - ASTM F1978 Taber Abrasion (passed)
    - ASTM B571 Impact, Chisel/Knife, Peel (passed)

Taber abrasion

Impact/Adhesion

Corrosion

Corrosion

Cr

nCoP

X

Y

0 Hrs

480 Hrs

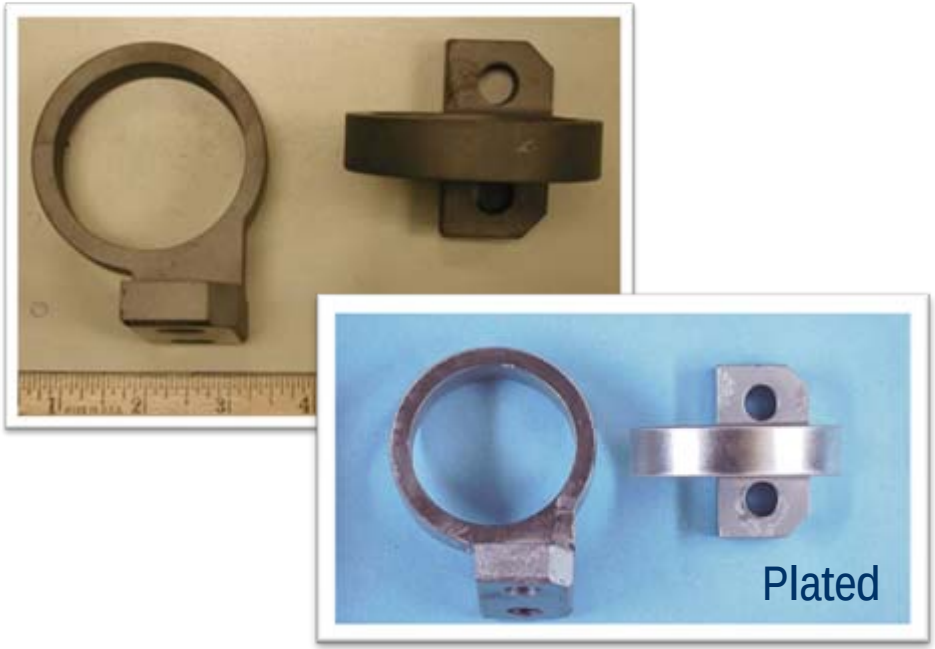
Rig Test

Nanovate™ CR (center)

Component Producibility
NAVSEA Refueling Parts

NAVSEA – NESDI Leveraged Effort

- **Refueling At Sea Components (Norfolk Naval Shipyard)**



4340 Steel Bearing Housings

17-4 PH Stainless Roller Shafts

Component Producibility
Boeing Aircraft Parts

Boeing Seattle – Aircraft Components

- **Boeing Producibility Items**

737 Trunnion Pin – 4340M

787 Drive Shaft – 4340M

Component Producibility
Landing Gear

Messier Dowty – V-22 Components

- **Messier-Dowty Producibility Items**

V-22 NLG Piston

V-22 Osprey

Commercial Uses
Prototyping & Development

- **Integran Technologies, Inc. (Toronto Canada)**
  - Nanovate CR prototyping line in operation since 2004
  - 600 gallon Plating Tank
  - In-line activation tanks
    - Mild steel, alloy steels, stainless steels, aluminum, Inconel, nickel…
  - JTP sample production
  - Commercial prototyping
    - Hydraulics, valves, pistons, shocks, engines, actuators, landing gear…
    - OEM and R&O

600 gal Plating tank at Integran (2010)

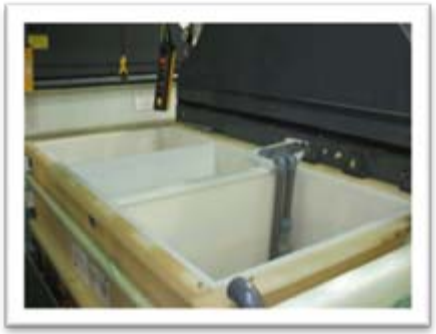
Commercial Uses
Enduro Industries, Inc.

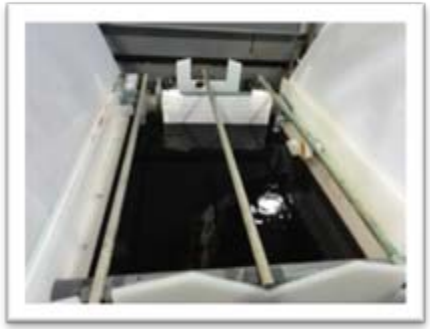
- **Enduro Industries, Inc. (Hannibal, MO)**
  - Nanovate CR process line installed and in operation since 2008
  - Applying Nanovate CR to mild and induction hardened steel bars for use in hydraulic actuators for fluid power
  - 700 gallon Plating Tank
  - Integran provides on-going support of line
  - Milestone: 1,000,000 Amp-hrs of production plating

Commercial Uses P&WC

- **Pratt & Whitney Canada (Longueil, Canada)**
  - EHC replacement for R&O of engine components
  - Retrofit equipment to convert to Nanovate™ CR Dem/Val Process Line
  - Process line in use since Nov 2010
  - 250 gallon Plating Tank

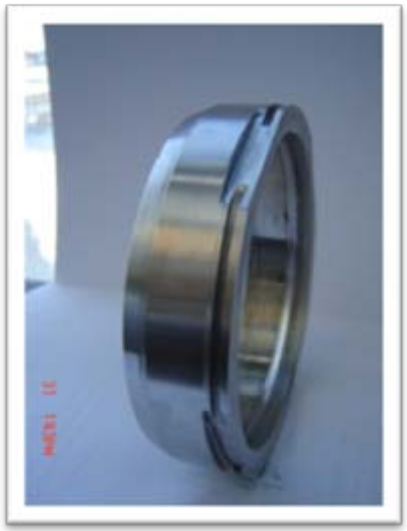
Support provided by:





Commercial Uses P&WC

- Demonstration components plated for PT6 platform (shown after machining):
  - Prop shaft
  - Seal runner



Seal runner plated at PWC (Jan 11)

Prop shaft plated at ITI (Oct 10)

Prop shaft plated at PWC (Jan 11)

Turbo Prop PT6

Summary

- **Nanovate CR (nCo-P):**
  - Environmentally compliant EHC alternative
  - Process compatible with existing plating infrastructure
  - Reduced energy consumption, increased throughput
  - Production process in commercial use (TRL 7)
- **Nanovate CR Material Properties**
  - Enhanced corrosion and wear
  - Non-embrittling
  - Improved fatigue performance vs. EHC
- **Future work (WP-0936)**
  - Performance testing (JTP)
  - Dem/Val at NAVAIR JAX Depot
  - OEM Producibility Components

For more information…

NAVAIR

INTEGRAN TECHNOLOGIES INC.

Visit our booth at ASETS Defense

Questions

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BACKUP MATERIAL

IH Assessment at NAVAIR JAX

- NAVAIR-JAX IH assessment on Co emission on the Dem/Val tank.

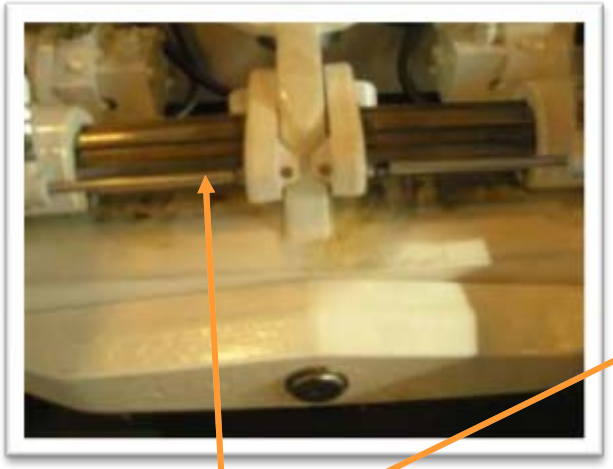
DATE:	PERSONAL SAMPLING RESULTS (8-HR TWAS)	AREA SAMPLING RESULTS (8-HR TWAS)	VENTILATION MEASUREMENTS (TAKEN ON THE PULL SIDE)	DRY BULB READINGS (2)	RELATIVE HUMIDITY (3)
8 Aug 2007	Below the LOD	0.0023 mg/m^3	3519 FPM	Initial: 79.1°F Final: 97.3°F	Initial: 100% Final: 58%
9 Aug 2007	Below the LOD	0.0074 mg/m^3	3545 FPM	Initial: 81.2°F Final: 97.6°F	Initial: 100% Final: 58%
16 Aug 2007	Below the LOD	0.0017 mg/m^3	4001 FPM	Initial: 79.0°F Final: 94.4°F	Initial: 91% Final: 51%
22 Aug 2007	Below the LOD	Below the LOD	4366 FPM	Initial: 78.5°F Final: 95.0°F	Initial: 94% Final: 50%
24 Aug 2007	Below the LOD	Below the LOD	4088 FPM	Initial: 77.5°F Final: 94.2°F	Initial: 100% Final: 58%

Co PEL is 20 µg/m^3

Dem/Val Component
Spread Cylinder Hydraulic Rod

NAVAIR Lakehurst – Ground Support Equipment

- Spread Cylinder Hydraulic Rod
  (A/S32A-32 Aircraft Towing Tractor “Spotting Dolly”)
- Supply System Risk



Spread Cylinder Rod in Assembly

Actuator Assembly

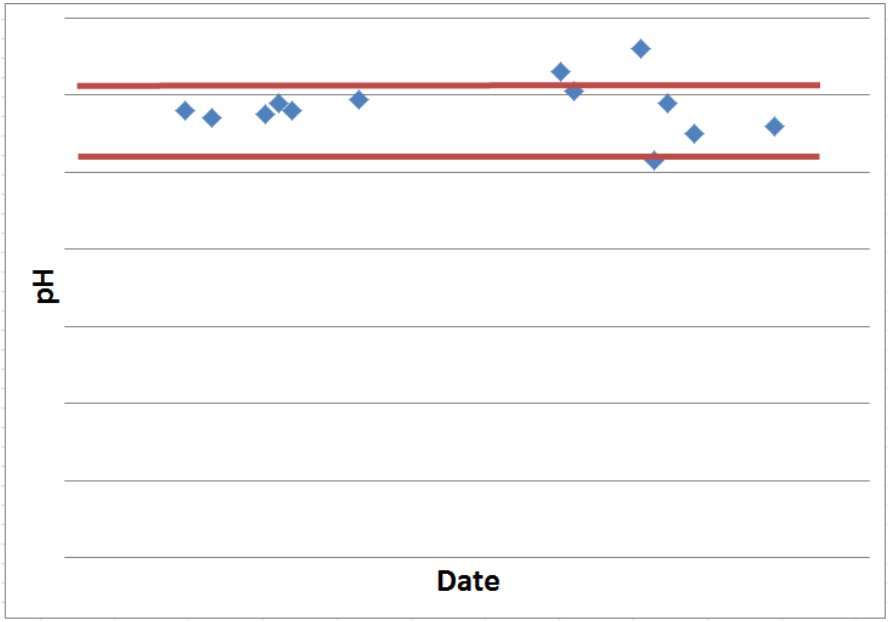
Two Different Sizes Shown

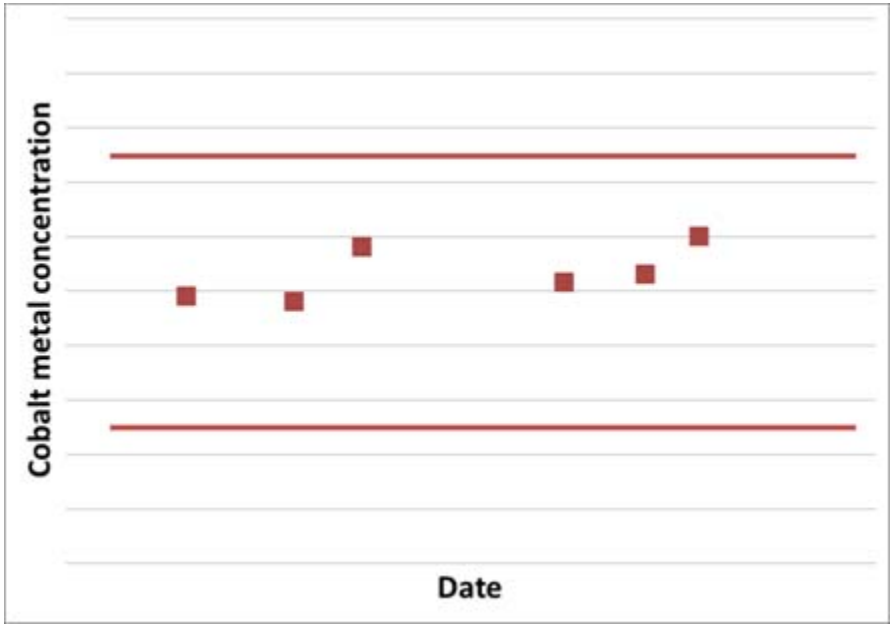
Coating Properties

Nanovate™ CR

		Nanovate CR	EHC
Appearance		Pit, Pore, Crack -free	Microcracked
Ductility		2-7%	<1%
Hardness	*As-Deposited*	530-600 VHN	Min. 600 VHN
	Heat Treated	750 VHN	-
Adhesive Wear (Pin-on-disk)	*Wear loss*	6-7 x 10^{-6} mm^3/Nm	9-11 x 10^{-6} mm^3/Nm
	Coefficient of friction	0.4-0.5	0.7
	Pin Wear	Mild	Severe
Corrosion †*ASTM B537 Rating*	*Salt Spray ASTM B117*	† Protection Rating 8 (1000 h) @ 0.002"	† Protection Rating 2 (1000 h) @ 0.004"
Hydrogen Embrittlement	*ASTM F519*	Pass with bake	Pass with bake
Fatigue	*Axial & Rotating Beam*	Credit vs. EHC Comparable to bare	Significant debit vs. bare

Commercial Uses P&WC



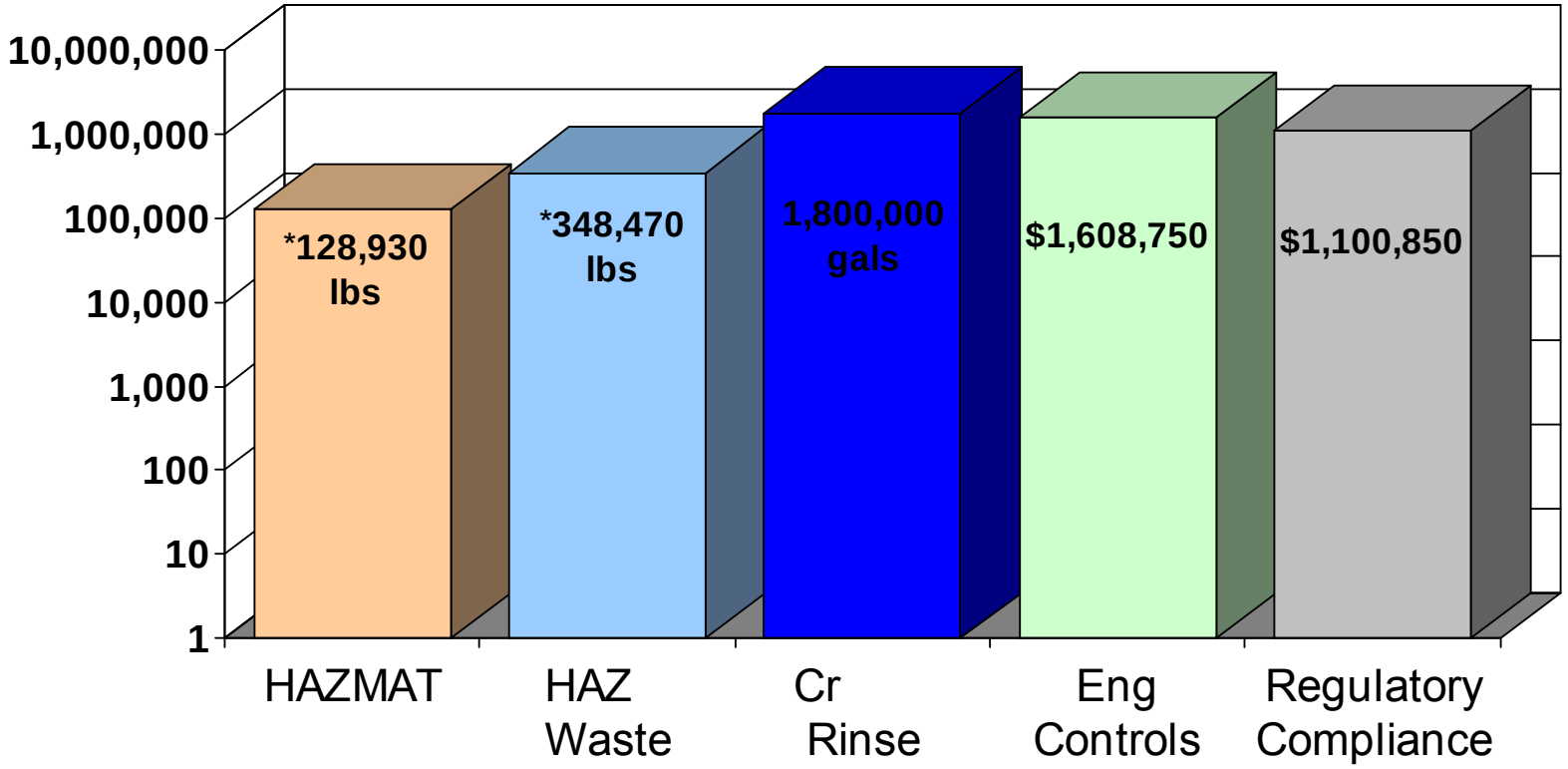


- Technology transfer underway
- Integran provides on-going support for the line
- Early process monitoring demonstrates good production control

Environmental Driver/Benefit

(Hexavalent Chromium Plating at Navy FRCs)

- **Estimated NAVAIR P2 Savings over 10 Yrs**



Note: the above projected savings are assumptions based on FRC-SE data extrapolated to other Navy FRCs

** Estimated amounts due to chrome plating based on average Environmental Systems Allocation (ESA) data extrapolated across all FRCs over a 10 yr period*

Cobalt
Environment & Worker Safety

Cobalt Air Emissions – US EPA (Environmental Protection Agency)

- Emission limit different by state
  - Typical emission limit without requiring a license is 0.1 tons per year
- EPA estimating tool employed to determine emissions
  - Variables for estimator – bath amps, bath operating hours
  - Typical results are less than 50 lbs (20kg) per year
  - Drivers size of parts being plated, number / shifts (amp hours)
- Nanovate CR emissions below limits

Aqueous System - Environmental

- Dust or fume not produced by the plating process
- Nano materials do not become airborne
  - Nano material plated directly onto the substrate material
  - No sprays to disperse nano materials in the atmosphere

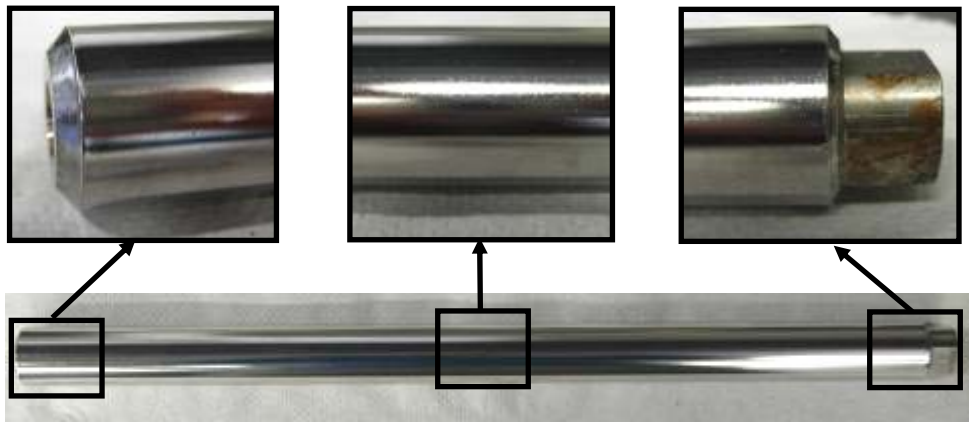
Cobalt Development Institute – Additional Information

- www.thecdi.com/cdi/images/documents/facts/Cobalt_Facts-HS&E.pdf

Highly Efficient Process Produces very little Cobalt emissions

Rod-Seal Wear Testing

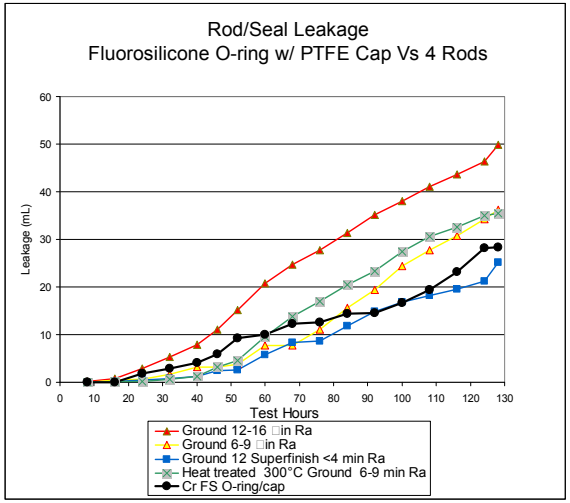
- Four PH 13-8Mo hydraulic actuator rods
  - Plated with 0.006-0.008” Nanovate CR
  - Hydrogen baked (375°F, 23h) or heat treated (300°C, 6 h)
  - Ground to 6-9 µinch, 12-16 µinch or superfinished to Ra < 4 µinch
- Testing conducted at NAVAIR-PAX
  - similar to ID cylinder wear - wear against seals
  - Tests showed Nanovate CR comparable to EHC

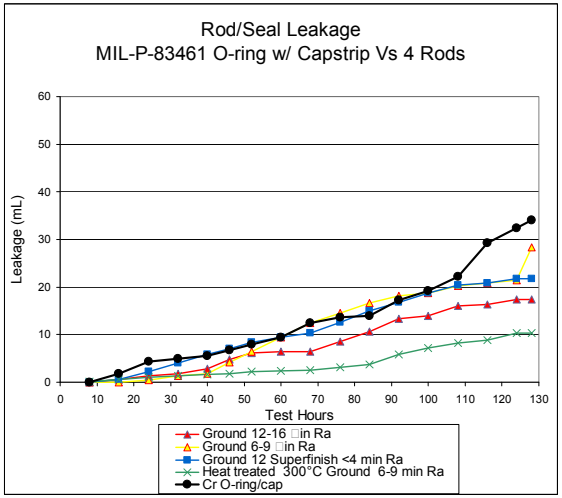


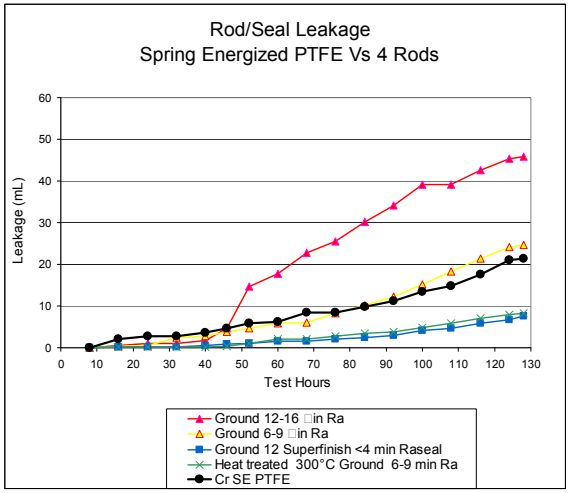
Nanovate CR coated hydraulic rod

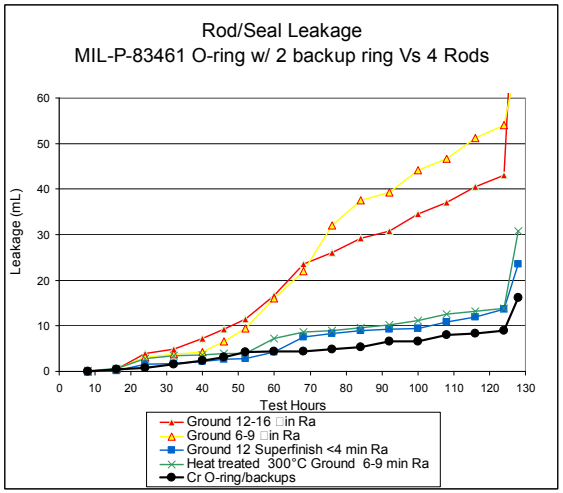
Rod-seal test apparatus

Rod-Seal Wear
(Leakage, Various O-rings)









Black lines hard chrome from prior HCAT work

- Different test run
- Nanovate CR roughly comparable with hard chrome
- Ground surfaces higher leakage

Joint Test Protocol

	Sample Production Progress	Sample Completion	Test Completion
Material Characterization	50%	Feb 2011	Mar 2011
Adhesion	0%	Feb 2011	
Fluid Immersion	100%	Feb 2011	
Corrosion	50%		Apr 2011
Adhesive Wear (PoD, BoR)	50%		
Abrasive Wear	0%		Mar 2011
Seal Wear	0%		
Gravelometry	0%		
Bushing Wear	0%		
Fatigue	0%		
Embrittlement	0%		

With support from Messier-Dowty SAFRAN Group